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Synthesis and structure of bis(2-*N*,*N*-dimethylamioethylselenolato)zinc and its transformation to ZnSe

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Abstract

The air-stable compound [$Zn(SeCH_2CH_2NMe_2)_2$] (**1**) as prepared from $Zn(OAc)_2 \cdot 2H_2O$ and 2 equiv. of $NaSeCH_2CH_2NMe_2$ contains monomeric molecules with a characteristically distorted tetrahedral zinc atom coordinated to two selenium and two nitrogen atoms. On thermolysis **1** yields ZnSe which was characterized by XRD.

Keywords: ZnSe; NMR; TGA; Structure

1. Introduction

Group II–VI compound semiconductors find extensive applications in modern technology [1,2], especially in blue light-emitting opto-electronic devices such as light-emitting diodes (LEDs) or laser diodes (LDs). Of the materials reported so far, ZnSe and GaN have been among the most promosing candidates. However, due to self-compensation and/or residual impurities in the former, it has been difficult to realise a p–n junction which is essential for a CW blue light-emitting diode [3,4]. For the development of ZnSe-based devices, the preparation of a p-doped material has been a major obstacle [4,5]. To overcome this problem a Group 11 element on the zinc site or a Group 15 element on the selenium site is usually employed. Plasma-activated nitrogen incorporation in ZnSe during MBE growth has been reported for the first time in the 1990s [6]. However, attempts to prepare nitrogen-doped ZnSe via chemical vapor deposition (CVD) techniques have led to unacceptably low concentrations of nitrogen [4]. This has been a motivation for the current interest in the development of suitable molecular precursors for CVD techniques improving the p-type doping efficiency. To address the doping problem we have recently designed a hybrid selenium–nitrogen alkyl ligand ($Me_2NCH_2CH_2Se^-$) [7] which may provide acceptable levels of nitrogen following the thermal decomposition of corresponding metal complexes.

2. Experimental

The reactions were carried out in dry and distilled analytical grade solvent. $Zn(OAc)_2 \cdot 2H_2O$ was obtained from commercial source. Melting point was determined in capillary tubes and are uncorrected. Elemental analyses were carried out by the Analytical Chemistry Division of B.A.R.C. ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47 MHz, respectively. Chemical shifts are relative to the internal chloroform peak at δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C. Thermogravimetric analyses (TGA) were carried out on a Setaram 92-16-18 instrument which was calibrated with $CaC_2O_4 \cdot H_2O$. The TG curves were recorded at a heating rate of

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3 °C min^{-1} under a flow of argon. X-ray powder diffraction was measured using Cu Kα radiation.

2.1. Preparation of [$Zn(SeCH_2CH_2NMe_2)_2$]

To a freshly prepared methanolic solution (3 cm^3) of $NaSeCH_2CH_2NMe_2$, (prepared from $(Me_2NCH_2CH_2Se)_2$ [7] (118 mg, 0.39 mmol) in MeOH (5 cm^3) and a dilute methanolic solution of $NaBH_4$ (31 mg, 0.81 mmol)) was added a CH_2Cl_2 suspension of $Zn(OAc)_2 \cdot 2H_2O$ (86 mg, 0.39 mmol). The colourless solution was stirred for 3 h under N_2. The solvents were stripped off in vacuo and the residue was extracted with CH_2Cl_2 (3 × 10 cm^3) and passed through a short Florisil column. The volume was then reduced to 3 cm^3 under vacuum and C_6H_{14} (5 cm^3) was added. On cooling at −10 °C the clear solution gave colourless crystals of [$Zn(SeCH_2CH_2NMe_2)_2$] (93 mg, 65%). M.p. 158 °C. *Anal.* Calc. for $C_8H_{20}N_2Se_2Zn$: C, 26.1; H, 5.5; N, 7.6. Found: C, 25.9; H, 5.7; N, 7.5%. ^1H NMR ($CDCl_3$ 25 °C) δ: 2.42 (s, NMe_2); 2.65 (m, CH_2CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 25 °C) δ: 12.6 (s, $SeCH_2$); 45.4 (s, NMe_2); 63.5 (s, NCH_2).

2.2. X-ray crystallography

Experiment was similar as in Ref. [12].

3. Results and discussion

The title complex [$Zn(SeCH_2CH_2NMe_2)_2$] (**1**) was prepared by the reaction of $Zn(OAc)_2 \cdot 2H_2O$ with two equivalents of $NaSeCH_2CH_2NMe_2$ in methanol/dichloromethane (Eq. (1)). The complex was isolated as a colourless, air-stable, monomeric species which is soluble in common organic solvents.

$$Zn(OAc)_2 \cdot 2H_2O + 2NaSeCH_2CH_2NMe_2 \rightarrow [Zn(SeCH_2CH_2NMe_2)_2] + 2NaOAc + H_2O \qquad (1)$$

The crystal structure of [$Zn(SeCH_2CH_2NMe_2)_2$] (**1**) as determined by X-ray crystallography [8] contains discrete molecules as shown in Fig. 1. The central zinc ion is coordinated to two non-planar five-membered chelating aminoselenolate ligands. The coordination geometry around zinc is that of a characteristically distorted 'flattened tetrahedron' as is typical for d^{10} centers with two unsymmetrically bidentate ligands (coordination number 2+2 [9,10]). The Zn–Se and Zn–N distances are similar to literature values [2,11]. Although the structure of **1** qualitatively resembles its sulfur analogue [$Zn(SCH_2CH_2NMe_2)_2$], the latter has two crystallographically independent molecules, differing slightly in bond distances and angles [10].

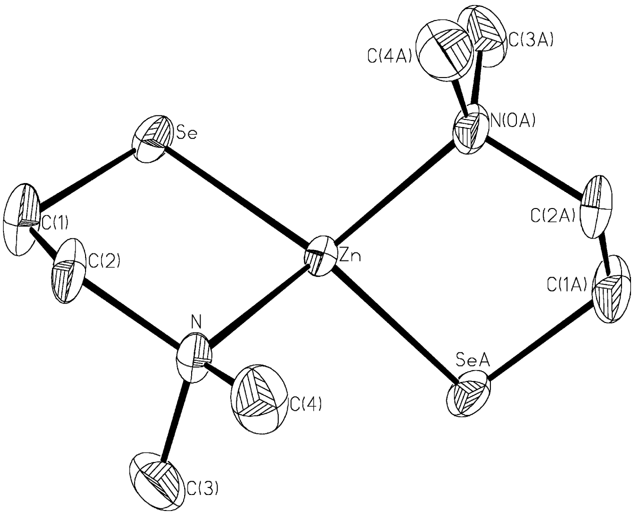

Fig. 1. ORTEP representation of [$Zn(SeCH_2CH_2NMe_2)_2$]. Selected bond distances (Å) and bond angles (°): Zn–Se 2.3864(9), Zn–N 2.119(6), Se–C 1.968(9), N(OA)Zn–N 117.5(4), N(OA)Zn–Se 110.33(17), N–Zn–Se 91.78(17), Se–Zn–Se(A) 137.23(7).

To assess the suitability of **1** for the preparation of ZnSe, a thermogravimetric analysis (Fig. 2) was carried out. The TG response showed that the complex decomposes via at least two overlapping decomposition routes, leading finally at 260 °C to ZnSe (from weight loss and XRD pattern [11]). To prepare larger quantities of ZnSe, substantial amounts of the complex were heated in a furnace at 320 or 450 °C under Ar or Ar/H_2 flow. The ZnSe formed under Ar or Ar/H_2 gas flow showed similar properties. However, the product formed at lower temperatures (320 °C) was highly contaminated with carboneous material. The product prepared at 450 °C showed low carbon contents (*Anal.* Found: Zn, 41.1; Se, 53.7; C, 0.7; H, <0.2; N, <0.2. Calc. for ZnSe: Zn, 45.3; Se, 54.7%). The XRD patterns for the products obtained from furnace heating and TG residue were comparable.

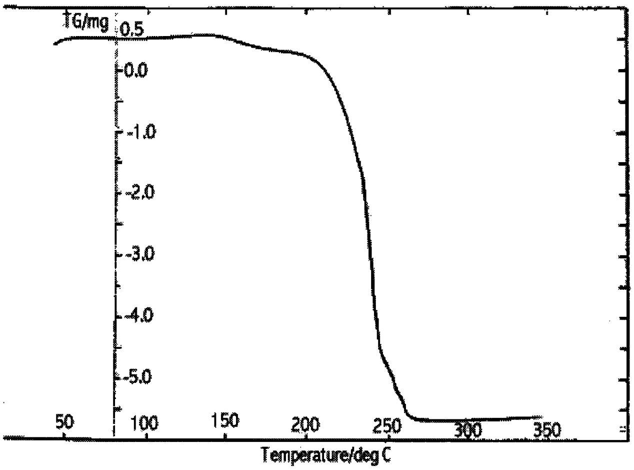

Fig. 2. TG curve of [$Zn(SeCH_2CH_2NMe_2)_2$].

The above results demonstrate that ZnSe can be obtained conveniently from the monomeric air-stable molecular precursor [Zn($SeCH_2CH_2NMe_2$)$_2$].

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